



TITLE:

<Division of Synthetic Chemistry>Organoelement Chemistry

AUTHOR(S):

CITATION:

<Division of Synthetic Chemistry>Organoelement Chemistry. ICR Annual Report 2012, 19: 4-5

ISSUE DATE:

2012

URL:

<http://hdl.handle.net/2433/172601>

RIGHT:

Division of Synthetic Chemistry – Organoelement Chemistry –

<http://boc.kuicr.kyoto-u.ac.jp/www/index-e.html>



Prof

TOKITOHI, Norihiro
(D Sc)



Assoc Prof

SASAMORI, Takahiro
(D Sc)



Assist Prof

MIZUHATA, Yoshiyuki
(D Sc)



Assist Prof *

AGOU, Tomohiro
(D Sc)



Techn Staff

HIRANO, Toshiko



PD

MIYAKE, Hideaki
(D Sc)



PD

MAYER, F. J. Ulrich
(Ph D)



PD

SUGAMATA, Koh
(D Sc)

* Also serves as Assist Prof of
Pioneering Research Unit for Next
Generation

Students

SAKAGAMI, Michiyasu (D3)
MIYAMOTO, Hisashi (D2)
EGAWA, Yasunobu (D1)

WASANO, Tatsuya (D1)
NAGATA, Koichi (M2)
TSUTSUMI, Yosuke (M2)

AWANE, Hiroyuki (M1)
IKEDA, Shin (M1)
KANESATO, Shuhei (M1)

Visitors

Prof LIPPOLIS, Vito
Prof APELOIG, Yitzhak
Prof SCHESCHKEWITZ, David

Department of Inorganic Chemistry, The University of Cagliari, Italy, 21 March
Department of Chemistry, Technion, Israel Institute of Technology, Israel, 16 October
Department of Chemistry, Faculty 8: Natural Sciences and Technology III, Saarland-
University at Saarbrücken, Germany, 16–17 October
School of Chemistry, University of Bristol, U.K., 19 November
Department of Chemistry, University of North Texas, U.S.A., 26 November

Prof RUSSEL, Chris
Prof BORDEN, Weston Thatcher

Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of “dreams” for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivities between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry.

KEYWORDS

Steric Protection
Kinetic Stabilization
Low-coordinated Species
Heteroatom
Transition Metal Complexes

Selected Publications

Miyake, H.; Sasamori, T.; Tokitoh, N., Synthesis and Properties of 4,5,6-Triphospha[3]radialene, *Angew. Chem. Int. Ed.*, **51**, 3458-3461 (2012).
Agou, T.; Sugiyama, Y.; Sasamori, T.; Sakai, H.; Furukawa, Y.; Takagi, N.; Guo, J. D.; Nagase, S.; Hashizume, D.; Tokitoh, N., Synthesis of Kinetically Stabilized 1,2-Dihydrodisilenes, *J. Am. Chem. Soc.*, **134**, 4120-4123 (2012).
Sugamata, K.; Sasamori, T.; Tokitoh, N., Generation of an Organotellurium(II) Cation, *Eur. J. Inorg. Chem.*, 775-778 (2012).
Sasamori, T.; Sakagami, M.; Niwa, M.; Sakai, H.; Furukawa, Y.; Tokitoh, N., Synthesis of a Stable 1,2-Bis(ferrocenyl)diphosphene, *Chem. Commun.*, **48**, 8562-8564 (2012).
Agou, T.; Nagata, K.; Sakai, H.; Furukawa, Y.; Tokitoh, N., Synthesis, Structure, and Properties of a Stable 1,2-Dibromodialumane(4) Bearing a Bulky Aryl Substituent, *Organometallics*, **31**, 3806-3809 (2012).

4,5,6-Triphospha[3]radialene

Radialenes are a unique class of unsaturated hydrocarbons and have attracted much attention from the viewpoint of their cross-conjugated π -electron electronic structures. On the other hand, it was found that P=C bonds have unique characteristics that are different from those of C=C bonds, for example, they have lower LUMO levels relative to compounds with N=N or C=C double bonds. These unique characteristics of radialenes and low-coordinated phosphorus compounds prompted us to research the chemistry of the phosphorus analogues of radialenes, which are an attractive research target as a result of the synergy between the unique nature of radialenes and P=C bonds. We have succeeded in the synthesis of a stable 4,5,6-triphospha[3]radialene. The compound can be easily handled in air under ambient conditions, despite the [3]radialene moiety containing P=C bonds, and exhibits red-shifted absorption as well as high electron-accepting ability. The unique electronic properties are brought about by the synergistic effect of the [3]radialene framework and the phosphorus substitution.

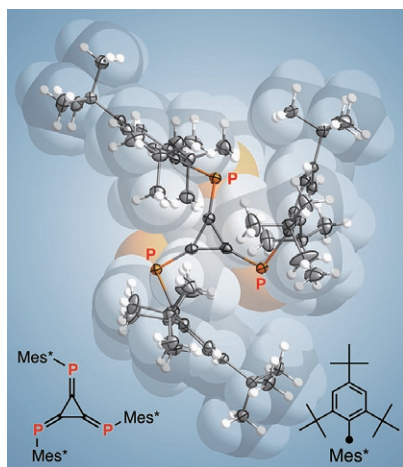


Figure 1. Structure of 4,5,6-triphospha[3]radialene.

1,2-Dihydrodisilenes

Despite the recent progress in the chemistry of kinetically stabilized multiply bonded silicon compounds, stable disilenes bearing more than one hydrogen substituent still remain elusive. Synthetically, the key challenge for the successful isolation of such multiply hydrogen-substituted disilenes lies in the effective stabilization of the sterically exposed H-Si=Si-H moiety. We have succeeded in the synthesis and isolation of the first stable 1,2-dihydrodisilenes by the introduction of sterically bulky aryl groups (Bbt and Bbp). These 1,2-dihydrodisilenes exhibit distinct Si=Si double-bond character in both solution and the

solid state. The Si-H bonds in these 1,2-dihydrodisilenes exhibit higher s character than those of typical σ^4, λ^4 -hydrosilanes.

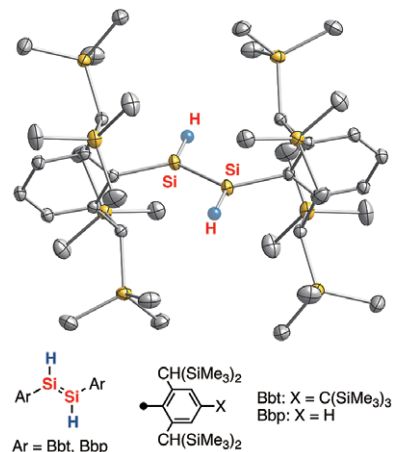


Figure 2. Structure of 1,2-dihydrodisilene.

1,2-Bis(ferrocenyl)diphosphene

Some d- π electron systems with two ferrocenyl (Fc) groups bridged by a π -bond moiety, *e.g.*, Ph(Fc)C=C(Fc) Ph or Fc-N=N-Fc have been reported and they show the unique properties of multi-step redox systems. A still prevailing limitation for the π -electron systems in these compounds is the restriction to the 2nd row of the p-block elements. We have succeeded in the synthesis and characterization of a stable 1,2-bis(ferrocenyl)diphosphene, wherein a P=P π -bond connects two ferrocenyl units. This represents an unprecedented example for a d- π electron system containing a heavier pnictogen π -spacer group. Stabilization of the highly reactive P=P π -bond was achieved by steric protection using two bulky ferrocenyl moieties. The assessment of its structural parameters and physical properties allowed the conclusion that the P=P π -bond is stable both in the solid state and solution and can act as an efficient π -electron spacer to couple the d-electrons of two ferrocenyl groups.

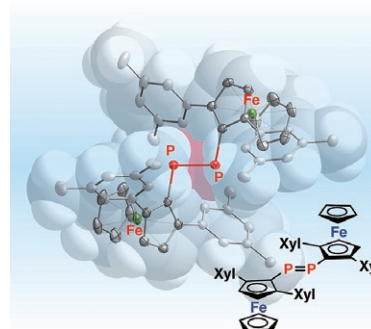


Figure 3. Structure of 1,2-bis(ferrocenyl)diphosphene. Xyl=3,5-dimethylphenyl.